Final Report

Title: **Computational Design, Theoretical and Experimental Investigation of Carbon anotube (CNT) - Metal Oxide /Metal Hydride Composite - A practicable Hydrogen storage medium for Fuel Cell - 3.**

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14. ABSTRACT **The results of hydrogenation of single walled carbon nanotubes (SWCNTs)-SnO2 composite, SWCNTs-WO3 composite, and SWCNTs-TiOs, are reported. The amount of hydrogen incorporated in the SWCNTs composites was determined and the dehydrogenation behavior was studied. The experimental evidences were provided by TEM, AFM, XRD, EDS, CHN and TG/TDS analyses.**

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Theoretical Investigation
First Principles Study of Hydrogen Storage in SWCNT Functionalized with metal complexes (MgH$_2$, TiO$_2$ & SnO$_2$)

Introduction

As the need for alternative energy is keep on increasing, the solid state storage of hydrogen remains a promising method for future energy needs. Due to their high surface area and stability carbon nanostructures are widely being investigated for storage purpose. Due to the poor hydrogen storage capacity of pristine carbon nanotubes, functionalization of carbon nanotube (CNT) is needed in order to become a nominal hydrogen storage medium (HSM) and to satisfy the US-DOE target. Based on our work on CNT+ BH3 [1,2] and other Hydrides[3-9] , in the present work, hydrogen storage in (10,10) armchair single walled carbon nanotube (SWCNT) functionalized with some metal complexes (Magnesium hydride (MgH$_2$), Titanium dioxide (TiO$_2$) and Tin dioxide (SnO$_2$)) has been investigated theoretically.

METHOD OF CALCULATION

All the calculations are carried out using density functional theory (DFT) as implemented in VASP. The projector augmented wave (PAW) potentials are used with local density approximation (LDA). Two unit cells of SWCNT (10, 10) are considered in the simulation cell of dimensions 30 Å x 30 Å x 2c, where 'c' is the lattice constant along the tube axis. The Monkhorst-Pack scheme has been used with 1 x 1 x 8 k-points. The electronic band structure and the density of states (DOS) are calculated using 21 k-points scheme. As a beginning, single molecule of MgH$_2$ (TiO$_2$, SnO$_2$) is attached to the CNT. The molecules are attached at a large distance in the outer surface of CNT and allowed to relax. After the interaction of molecule with the tube is analyzed, eight of each respective molecules are attached to SWCNT (10,10) as a full coverage. These systems are denoted as C8MgH$_2$, C8TiO$_2$ and C8SnO$_2$ respectively. The H$_2$ molecules are attached one by one in these relaxed structures and for each system, the storage capacity, binding energy (E$_B$) per H$_2$ molecule, desorption temperature (T$_D$) has been calculated.

CNT+MgH$_2$ SYSTEM

Magnesium hydride (MgH$_2$) has been identified as a suitable material for hydrogen storage applications due to its light mass, high energy density, hydrogen storage capacity and abundance in nature. The bond length Mg-H is 1.54 Å.

RESULTS AND DISCUSSION

Figure 1a shows the relaxed structure of CMgH$_2$. It is noted that the CNT–MgH$_2$ distance and Mg-H bond lengths have increased to 2.73 and 1.72 Å respectively. The binding energy (E$_B$) of MgH$_2$ with CNT is found to be 0.46 eV, which ensures the thermodynamical stability of the system.
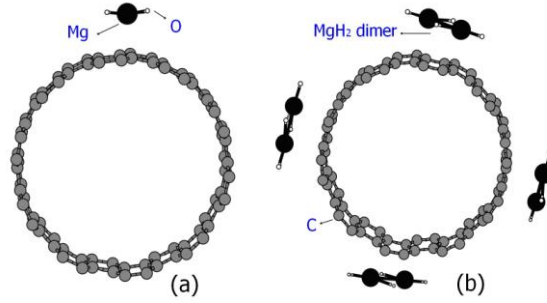
FIGURE 1. Single and eight MgH$_2$ molecules attached C(10,10).

As a full coverage, 8MgH$_2$ molecules have been attached to SWCNT(10,10). In this case, dimerization of MgH$_2$ molecules has observed (Fig. 1b), with an increased average Mg-H bond length (1.79 Å). The Mg-H bond lengths are not same in the relaxed structure and it is due to the different repulsive forces present in the dimer. The average H-H bond length in all the relaxed structures of H$_2$ molecules attached C8MgH$_2$ complex is about 0.78 Å (initial value = 0.74 Å). This notable change in H-H bond length ensures the strong interaction of H$_2$ molecules with C8MgH$_2$.

TABLE 1. H$_2$ binding energy, desorption temperature and storage capacities in all hydrogenated systems of C8MgH$_2$.

System	Binding energy per H$_2$ molecule (eV)	Desorption Temperature (K)	wt.% of H$_2$
CNT + 8(MgH$_2$+H$_2$)	0.28	357.39	1.36
CNT + 8(MgH$_2$+2H$_2$)	0.21	265.65	2.68
CNT + 8(MgH$_2$+3H$_2$)	0.55	703.28	3.97
CNT + 8(MgH$_2$+4H$_2$)	0.32	405.31	5.22
CNT + 8(MgH$_2$+5H$_2$)	0.34	434.44	6.44

The H$_2$ binding energy, desorption temperature and storage capacities in all hydrogenated systems of C8MgH$_2$ are given in Table 1. It can be noted that the H$_2$ binding energy range is 0.21 - 0.55 eV, whereas E$_B$ for MgH$_2$ in C8MgH$_2$ system is 1.12 eV. Hence, desorption of H$_2$ will not affect the CNT- MgH$_2$ complex. Also, the H$_2$ binding energy range is around the ideal range (0.2 − 0.4 eV) and hence, T$_D$ of H$_2$ molecules lies in the nominal range applicable for hydrogen based fuel cells used in mobile applications.
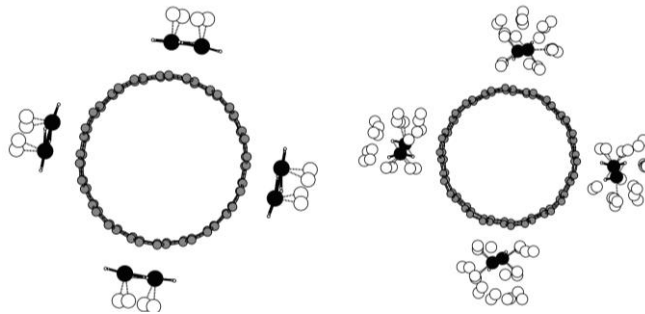

FIGURE 2. Single and five H$_2$ molecules attached in each MgH$_2$ of C8MgH$_2$

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Figure 2 shows the relaxed structures of C8MgH$_2$ after the adsorption of one and five H$_2$ molecules in each MgH$_2$. From the band structures (Fig. 3a), it may be noted that the number of valence bands increases by the addition of MgH$_2$ and the metallic nature of C(10,10) is not affected by MgH$_2$ functionalization. From the partial density of states (PDOS) plot (Fig. 3b) of C8MgH$_2$ one can infer that MgH$_2$ has strongly perturbed the CNT.
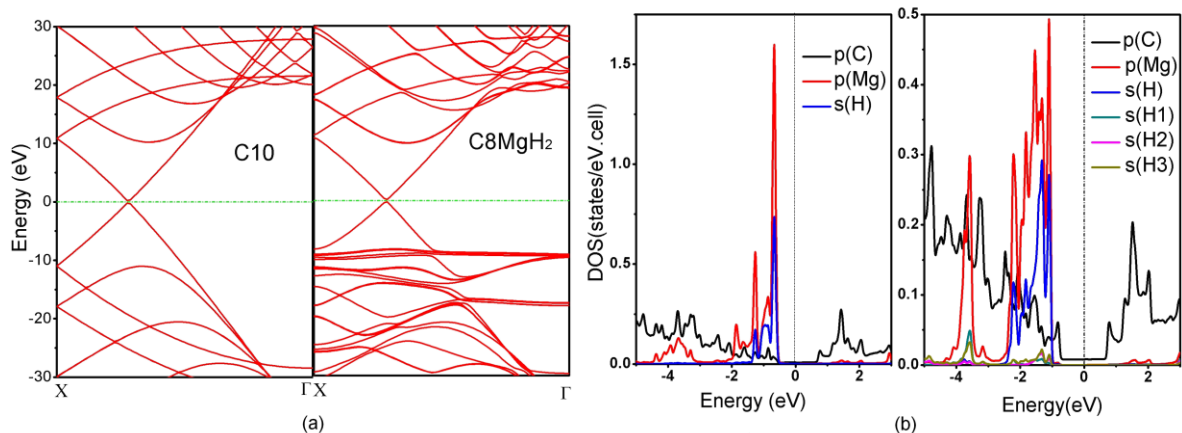

FIGURE 3. (a) Band structures of SWCNT (10,10) and C8MgH$_2$ (b) PDOS of C8MgH$_2$ and CNT + 8(MgH$_2$+3H$_2$)

The PDOS plot for CNT+8(MgH$_2$+3H$_2$) complex gives information on hybridization of s-orbital of adsorbed hydrogen atoms with the valence p-orbital of the carbon and magnesium atoms. This confirms the strong interaction of H$_2$ molecules with C8MgH$_2$.

CNT+ TiO$_2$ SYSTEM

The hydrogen uptake of TiO$_2$-impregnated CNTs has been studied by many and it is known that atomic hydrogen binds to the rutile surface of TiO$_2$, even at room temperature. Interestingly, hydrogen is able to diffuse in and out of the bulk TiO$_2$, effectively making it a possible hydrogen storage media. The bond length Ti – O is 1.9475 Å.

RESULTS AND DISCUSSION

The relaxed structures of CTiO$_2$ and C8TiO$_2$ are denoted in figure 4. In CTiO$_2$ structure, it is observed that the linear structure of TiO$_2$ has been changed and Ti – O bond lengths are not same. The system is stable with a binding energy of 3.56 eV. The desorption temperature of TiO$_2$ from CNT is 4548.83 K which ensures the high thermal stability of the system.
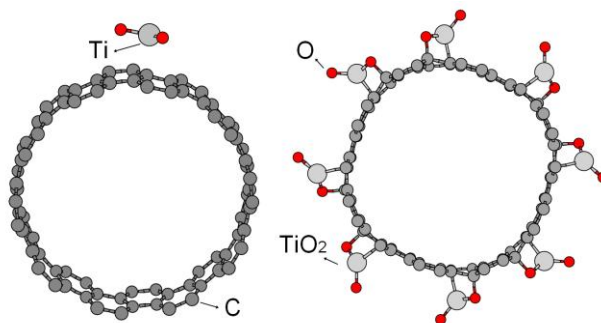
FIGURE 4. Single and eight TiO$_2$ molecules attached C(10,10).

Like CNT+MgH$_2$ system**,** 8 TiO$_2$ molecules are attached in the outer surface of CNT as shown in figure 4. The average binding energy per TiO$_2$ is found to be 3.27 eV. The average Ti $-$ O bond length is 1.77 Å, which is decreased from the initial value (1.94 Å). H$_2$ molecules are attached one by one in the relaxed structure (figure 5) and the average H $-$H bond length is found to decrease with each relaxation.
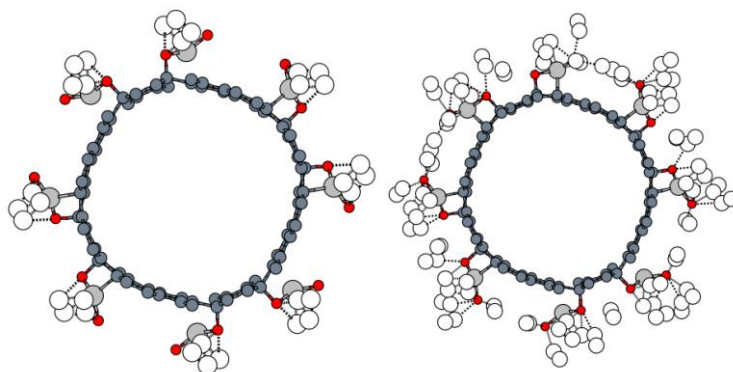

FIGURE 5. Two and six H$_2$ molecules attached in each TiO$_2$ of C8TiO$_2$

From table 2 it may be noted that the binding energy of the CNT + 8(TiO$_2$+H$_2$) system is beyond the nominal range (0.2 $-$ 0.4 eV) and due to its strong binding it can be desorbed from the C8TiO$_2$ complex only at high temperature (1065 K). All the other H$_2$ binding energies lie within the desired range and hence the system can serve as a good hydrogen storage medium. The C8TiO$_2$ system can hold up to 6 H$_2$ molecules in each TiO$_2$ and gives H$_2$ storage capacity of 5.7 wt%.

TABLE 2. H$_2$ binding energy, desorption temperature and storage capacities in all hydrogenated systems of C8TiO$_2$.

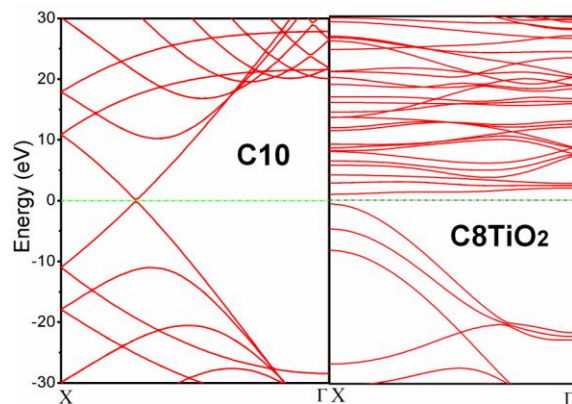| System	Binding energy per H$_2$ molecule (eV)	Desorption Temperature (K)	wt.% of H$_2$
CNT + 8(TiO$_2$+H$_2$)	0.83	1065.01	1
CNT + 8(TiO$_2$+2H$_2$)	0.39	496.67	1.98
CNT + 8(TiO$_2$+3H$_2$)	0.26	326.34	2.94
CNT + 8(TiO$_2$+4H$_2$)	0.24	300.53	3.88
CNT + 8(TiO$_2$+5H$_2$)	0.22	276.38	4.8
CNT + 8(TiO$_2$+6H$_2$)	0.22	275.49	5.7

FIGURE 6. Band structures of SWCNT (10,10) and C8TiO$_2$

From the band structure plots (figure 6) of C(10,10) and C8TiO$_2$ structures, one can note that the addition of TiO$_2$ molecules opens up a band gap at the 'X' point. The perturbation of TiO$_2$ molecules affect the metallic nature of the C(10,10) structure.
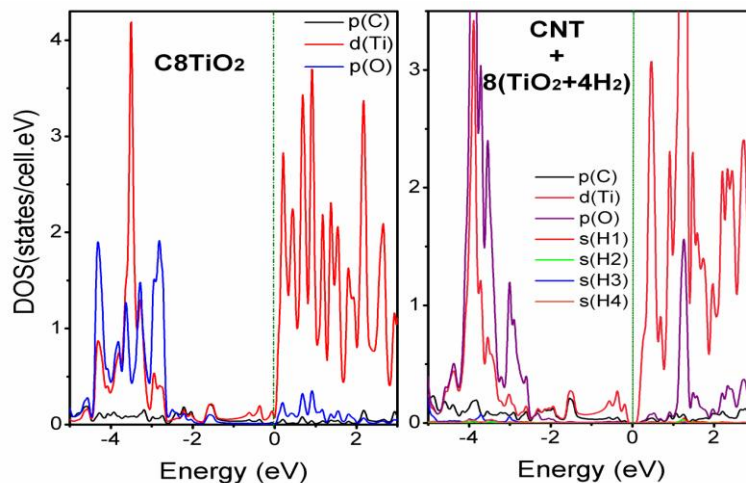

FIGURE 7. PDOS of C8TiO$_2$ and CNT + 8(TiO$_2$+3H$_2$)

The PDOS plot for CNT+8(TiO$_2$+3H$_2$) complex (figure 7) gives information on hybridization of s-orbital of adsorbed hydrogen atoms with the valence p-orbital of the carbon, d-orbital of titanium and s-orbital of the hydrogen atoms. This confirms the strong interaction of H$_2$ molecules with C8TiO$_2$.

CNT+ SnO$_2$ SYSTEM

SnO$_2$ nanoparticles (NPs) decorated CNTs are reported to be useful functional composites in many applications including gas sensors, fuel cells, batteries, and super capacitors. This is based on the fact that the work function of CNTs is approximately equal to that of SnO$_2$ allowing electrons to travel through the SnO$_2$ grains to CNTs and then be conducted in the CNTs with low resistance. The bond length Sn – O is 2.07 Å.

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RESULTS AND DISCUSSION

Figure 8 shows the relaxed structures of single and eight SnO_2 molecules attached C(10,10) structure and figure 9 illustrates one and three H_2 molecules attached in each SnO_2 of the relaxed C8SnO2 complex.
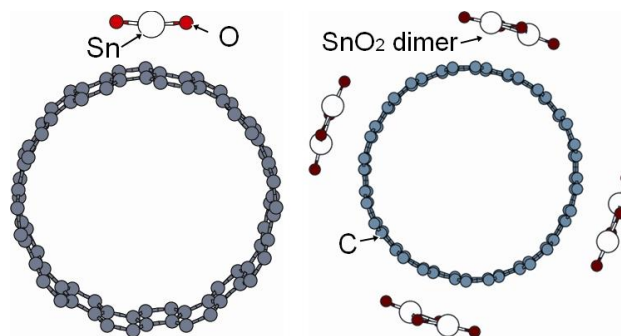

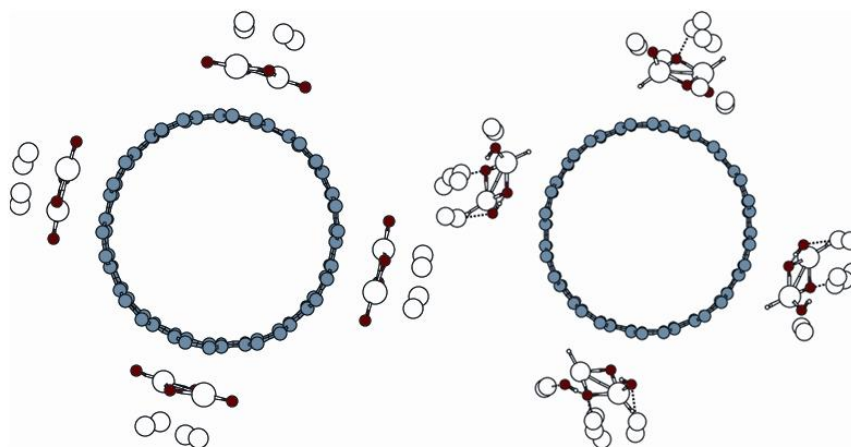**FIGURE 8. Single and eight SnO_2 molecules attached C(10,10).**

FIGURE 9. Single and three H_2 molecules attached in each TiO_2 of C8SnO2

SnO_2 molecule is attached in the C(10,10) SWCNT at a larger distance and allowed to relax. The binding energy of the single SnO_2 attached in CNT is 0.37 eV, whereas E_B per SnO_2 molecule in C8SnO2 system is 2.2 eV, indicates the system is highly stable one. Like the above systems H_2 molecules are attached one by one in the C8SnO2 complex. The values of binding energy per H_2 molecule, corresponding desorption temperature and H_2 storage capacity are summarized in table 3.

TABLE 3. H_2 binding energy, desorption temperature and storage capacities in all hydrogenated systems of C8SnO2.

System	Binding energy per H_2 molecule (eV)	Desorption Temperature (K)	wt.% of H_2
CNT + 8(SnO_2+H_2)	0.26	326.34	0.74
CNT + 8(SnO_2+2H_2)	0.26	326.34	1.47
CNT + 8(SnO_2+3H_2)	2.79	3564.95	2.18
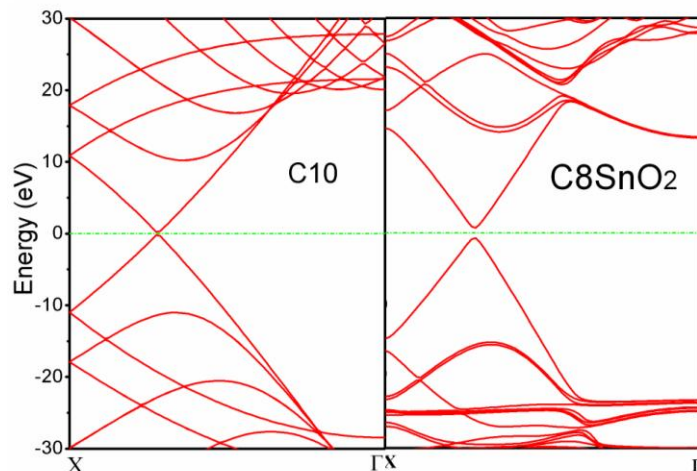
FIGURE 10. Band structures of SWCNT (10,10) and C8SnO$_2$

In this case also a small band gap opens in C(10,10) structure by the addition of SnO$_2$ molecules. This can be noted from the band structure plots (figure 10).

FIGURE 11. PDOS of C8SnO$_2$ and CNT + 8(SnO$_2$+3H$_2$)

The hybridization of valence p-orbitals of carbon, tin and oxygen atoms can be observed from the PDOS plot of C8SnO$_2$ system and the incorporation of valence s-orbital of the adsorbed hydrogen atoms in the C8SnO$_2$ complex can be seen the CNT + 8(SnO$_2$+3H$_2$) plot (figure 11)

CNT+ SnO$_2$+ TiO$_2$ SYSTEM

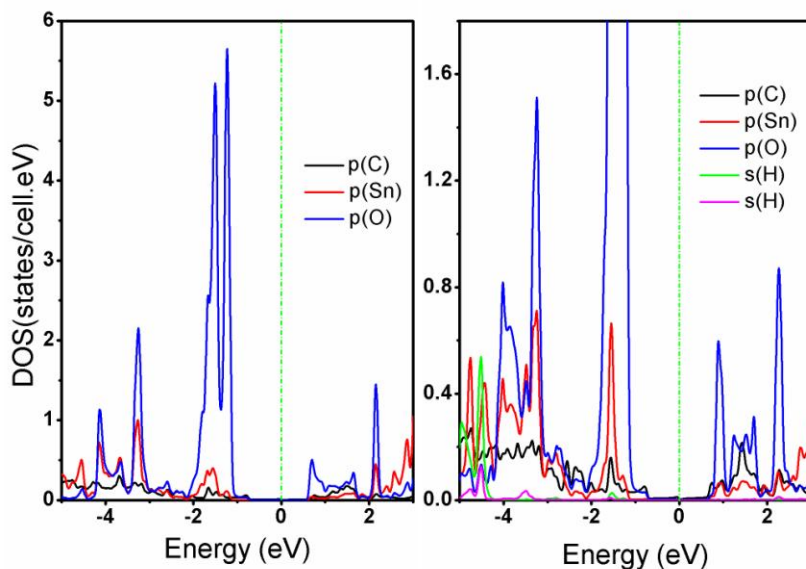It has also been tried to functionalize the SWCNT (10,10) with TiO$_2$ and SnO$_2$ nano complex. The TiO$_2$ and SnO$_2$ molecules are attached alternatively in the outer surface of the CNT. The relaxed structure of the fully covered CNT with SnO$_2$ and TiO$_2$ molecules is shown in figure12. H$_2$ molecules are attached one by one in the relaxed structure of the CNT+4SnO$_2$+4TiO$_2$ complex and the relaxed structure is depicted in figure 13.
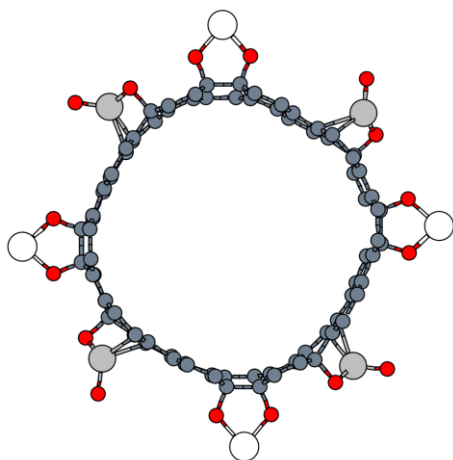
FIGURE 12. C(10,10) structure covered with 4SnO$_2$ and 4TiO$_2$ molecules
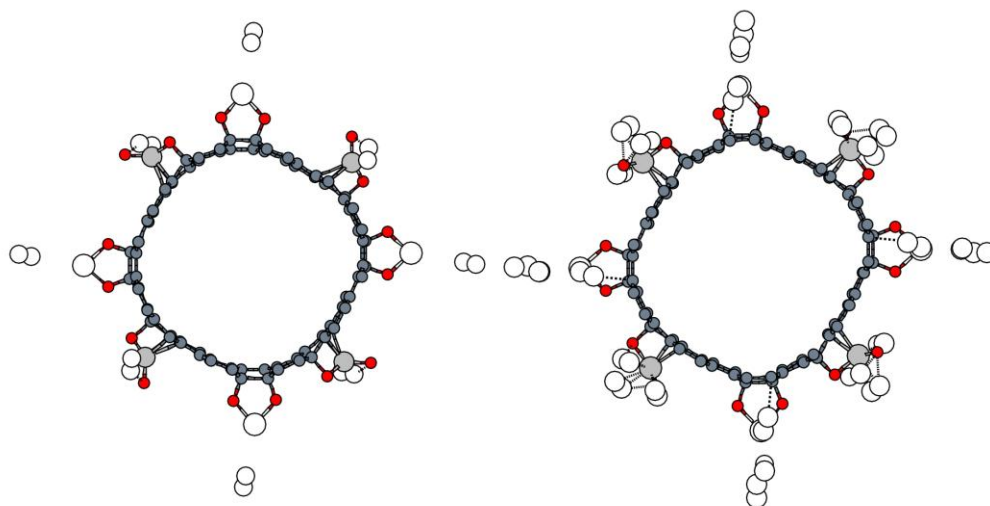
FIGURE 13. Single and three H$_2$ molecules attached in each SnO$_2$ and TiO2 of CNT+4SnO$_2$+4TiO$_2$

The values of E$_B$, T$_D$ and storage capacity of the H$_2$ storage in the CNT+4SnO$_2$+4TiO$_2$ complex are summarized in table 4. The binding energy values lie in the nominal range and hence H$_2$ molecules can be desorbed from the system at ambient conditions. The CNT + 8SnO$_2$+4TiO$_2$+24H$_2$ system gives storage capacity of 2.51 wt%.

TABLE 4. H$_2$ binding energy, desorption temperature and storage capacities in all hydrogenated systems of CNT+4SnO$_2$+TiO$_2$.

System	Binding energy per H$_2$ molecule (eV)	Desorption Temperature (K)	wt.% of H$_2$
CNT + 4SnO$_2$+4TiO2+8H$_2$	0.47	600.55	0.85
CNT + 8SnO$_2$+4TiO$_2$+16H$_2$	0.26	332.22	1.68
CNT + 8SnO$_2$+4TiO$_2$+24H$_2$	0.31	396.11	2.51

CNT+ SnO$_2$+ BH$_3$ SYSTEM

To improve the hydrogen storage capacity, in CNT+4SnO$_2$+4TiO$_2$ system, the TiO$_2$ (heavy transition metal oxide) is replaced by BH$_3$ molecule (light metal hydride). The relaxed structures of the fully covered CNT+ SnO$_2$+ BH$_3$ system is shown in figure 14. Two cases are considered for BH$_3$ functionalization in relaxed structure of C8SnO$_2$. One is BH$_3$ molecule is attached on the SnO$_2$ and the other one is on the surface of the carbon nanotube. The former one has binding energy of 3.8 eV and the later one has 2.34 eV. Then the system with larger binding energy (most stable system) is considered for storing hydrogen in it.
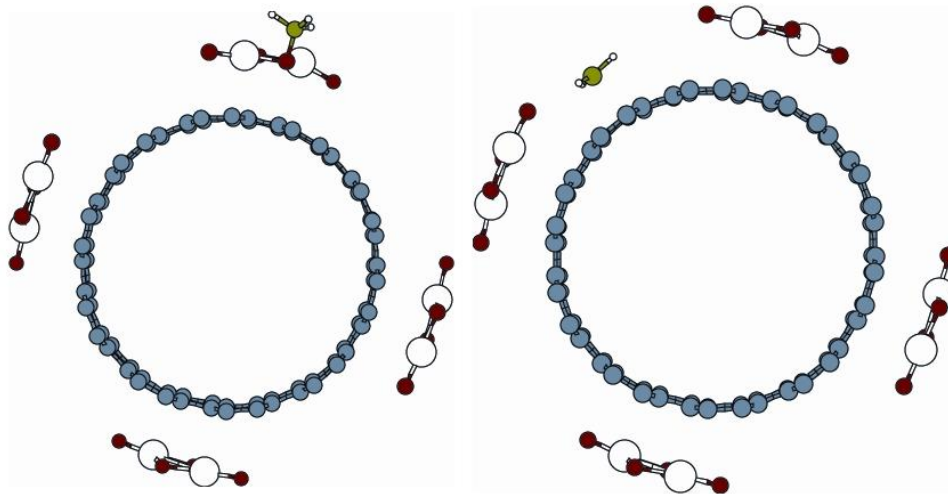

Figure 14. Relaxed structures of BH$_3$ attached on SnO$_2$ molecule and on CNT wall

References:

1. Aluminum hydride coated single-walled carbon nanotubes as a hydrogen storage medium
   K. Iyakutti, Y. Kawazoe, M. Rajarajeswari and V. J. Surya
   International Journal of Hydrogen Energy, 34 (2009) 370-375.

2. Functionalization of single walled carbon nanotube with borane for hydrogen storage
   V. J. Surya, **K. Iyakutti**, M.Rajarajeswari and Y. Kawazoe
   Physica E, 41 (2009) 1340-46.

3. Clustering of functional molecules on a single walled carbon nanotube surface and its effect on hydrogen storage
   K. Iyakutti, V. J. Surya, M. Rajarajeswari, N. S. Venkataramananan and Y. Kawazoe
   Phys. Stat. Sol. b 246 (2009) 2248-2256.

4. First-principles study on hydrogen storage in single walled carbon nanotube functionalized with ammonia,
   V. J. Surya, **K. Iyakutti**, M. Rajarajeswari and Y. Kawazoe,
   J. Comput. Theor. Nanosci. 7 (2010) 552-557.

5. The role of Li and Ni metals in the adsorbate complex and their effect on the hydrogen storage capacity of single walled carbon nanotubes coated with metal hydrides, LiH and NiH$_2$,
   V. J. Surya, **K. Iyakutti**, N.S. Venkataramanan, H. Mizuseki and Y. Kawazoe,
   Int. J. Hydrogen Energy 35 (2010) 2368 - 2376.

6. First principles investigation on carbon nanostructures functionalized with borane: An analysis on their hydrogen storage capacity**,**
   V. J. Surya, **K. Iyakutti**, V. Prasanna Venkatesh, H. Mizuseki and Y. Kawazoe,
   Physica E 43 (2011) 1528-1534/ doi: 10.1016/j.physe.2011.05.003

8. Single walled carbon nanotubes functionalized with hydrides as potential hydrogen storage media: A survey of intermolecular interactions,
   V. J. Surya, **K. Iyakutti** , N. S. Venkataramanan, H. Mizuseki , and Y. Kawazoe,
   Physica status solidi B, 248 (2011) 2147–2158 /DOI 10.1002/pssb.201046532

9**.** First principles study on desorption of chemisorbed hydrogen atoms from single-walled carbon nanotubes under external electric field
   V.J. Surya, **K. Iyakutti**, H. Mizuseki and Y. Kawazoe
   International Journal of Hydrogen Energy 36 (2011) 13645-13656.

Experimental Investigation

I. Hydrogenation in Single walled carbon nanotubes-SnO$_2$ composite

Abstract

The results of hydrogenation of single walled carbon nanotubes (SWCNTs)-SnO$_2$ composite thin film is reported here. SWCNTs mixed with SnO$_2$ by weight are made into pellet without any binder. Then, the pellet is evaporated by electron beam on glass substrates at room temperature in hydrogen atmosphere. The amount of hydrogen incorporated in the SWCNTs-SnO$_2$ composite is found to be 2.4 wt.%. In addition, the hydrogenation of pure SnO$_2$ material is carried out and its storage capacity is compared with SWCNTs-SnO$_2$ composite. The dehydrogenation behavior is also studied. The experimental evidences are provided by TEM, AFM, XRD, EDS, CHN and TG/TDS analyses. In the present study, we have reported the hydrogenation in SWCNTs-SnO$_2$ composite thin film prepared by electron beam technique for the first time. The electron-beam evaporation is one of the widely used techniques for preparing thin film with high quality and reproducibility.

1. Experimental

1.1. Composite preparation

SWCNTs are purchased from Sigma Aldrich with the purity of >98%. SnO$_2$ material with the minimum assay of 99% is purchased from Merck. The SWCNTs are mixed with SnO$_2$ in the ratio of 1:2 by weight. This mixture is grounded well for 15 min. using agate mortar, and is placed in a cylinder-shaped steel mould. Uni-axial pressure of 5 MPa is applied to make them into pellet. Pellet with a diameter of 15 mm and a height of about 5 mm is obtained.

1.2. Film deposition

Glass substrates of dimension 25mm × 75mm × 1.35mm are cleaned with chromic acid, acetone and distilled water by means of sonication for 30 min. The pellet is placed in water cooled graphite crucible and then evaporated in hydrogen atmosphere by electron beam (Hind Hivac Model – 12A4D) on glass substrates at room temperature. The distance between the electron beam source and the substrate is 20 cm. The chamber base pressure is 6×10^{-6} mbar before deposition. The vacuum chamber is flushed with hydrogen gas for 3 min. before evaporation. A beam voltage of 6 kV with the beam current of 20 mA is applied. The hydrogen gas is allowed at a flow rate of 0.5 lit/min. up to the vacuum level 5×10^{-5} mbar during evaporation and the evaporation duration is 15 min.

1.3. Beam production and Hydrogenation

The hydrogen gas is allowed through a regulated valve and gets atomized by thermal cracking produced by tungsten filament. The atomized and excited molecules of hydrogen gas emerge from the valve and impinge on the substrate along with the evaporant and thereby ensure the complete hydrogenation process. Two set of thin films of pure SnO_2 material and SWCNTs-SnO_2 composite in hydrogen atmosphere are prepared under same experimental conditions.

1.4. Characterization

The morphology of SWCNTs is studied by transmission electron microscopy (TEM). The morphology of pure SnO_2 and SWCNTs-SnO_2 composite thin film is studied by atomic force microscopy (AFM). The phases of the SnO_2 thin film is studied by X-ray diffraction (XRD) technique. Energy dispersive spectroscopy (EDS) is used to validate the presence of all elements in the SWCNTs-SnO_2 composite. CHN-elemental analysis is carried out to know the amount of hydrogen incorporated in pure SnO_2 and SWCNTs-SnO_2 composite thin film. The hydrogen desorption behavior is studied by thermo gravimetric/thermal desorption spectroscopy (TG/TDS) studies.

2. Results and Discussion

2.1. Morphology analysis

The morphology of SWCNTs is imaged by TEM analysis and is shown in Fig. 1(a). The image exhibits the high quality of SWCNTs with the average diameter of around 2 nm. Fig. 1(b) shows AFM image of pure SnO_2 thin film. It shows the good distribution of grains of SnO_2 with the average size of around 20 nm. The surface morphology of SWCNTs dispersed in SnO_2 thin film shown in Fig. 1(c). The AFM image reveals the inclusion of SWCNTs in SnO_2 thin film which results in the formation of circular cone protrusions on the smooth SnO_2 background. The three dimensional AFM image of SWCNTs-SnO_2 composite thin film is shown in Fig. 1(d). It shows the formation of the circular cone protrusion with the average height of around 50 nm. The width of the protrusion seems to be around 50 nm.
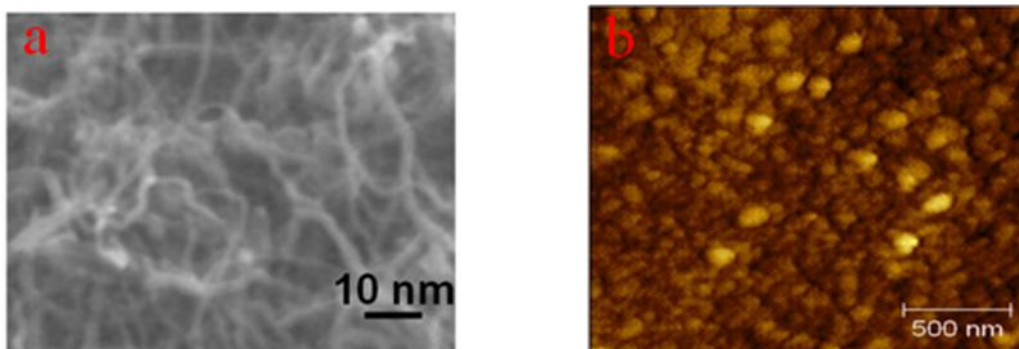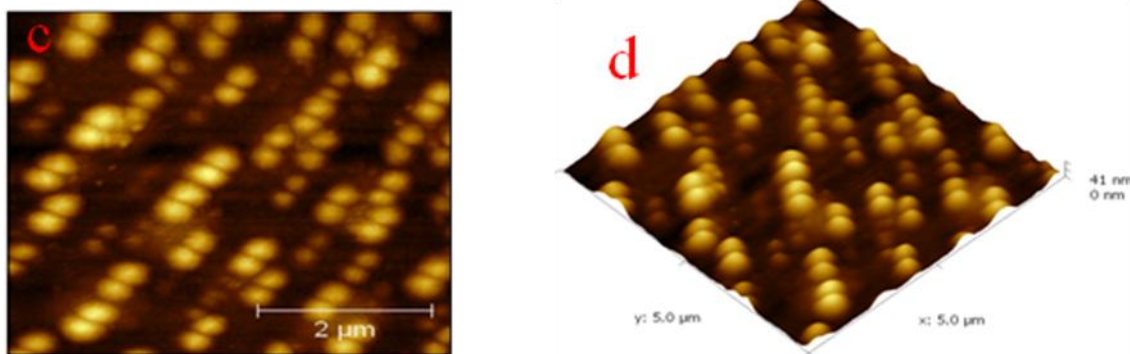
Figure 1: (a) TEM image of SWCNTs. (b) AFM image of SnO$_2$. (c) AFM image of SWCNT-SnO$_2$ composite. (d) 3D image of SWCNT-SnO$_2$ composite.

The SWCNTs in the composite may be aggregated due to the van der Waals forces to form the circular cone protrusion with the diameter in the obtained range. It is noted that from the AFM images, the CNTs are arranged perpendicularly to the plane of substrate rather the random arrangement on the SnO$_2$ thin film surface. The similar kind of occurrence of circular cone protrusion of MWCNTs on SnO$_2$ thin film background is obtained by Wisitsoraat *et al.* [1]. They pointed out that, the possible reason for this effect is that the CNTs self-organized themselves while they are moving toward substrates in line with the material evaporation trajectory, which is almost perpendicular to the substrate. Thus, the results expose that the deposition of SWCNTs with SnO$_2$ material is possible without any significant decomposition of SWCNTs. Further, the SWCNTs have systematic arrangements on SnO$_2$ thin film with the specific configuration, the circular cone protrusion.

2.2. XRD analysis

X-ray diffraction (XRD) analysis was performed on XPERT-PRO diffractometer operating at 40 kV and 30 mA, using Cu Kα radiation in the scanning range 2θ: 10°−80°. The diffraction pattern of pure SnO$_2$ thin film is shown in Fig. 2.
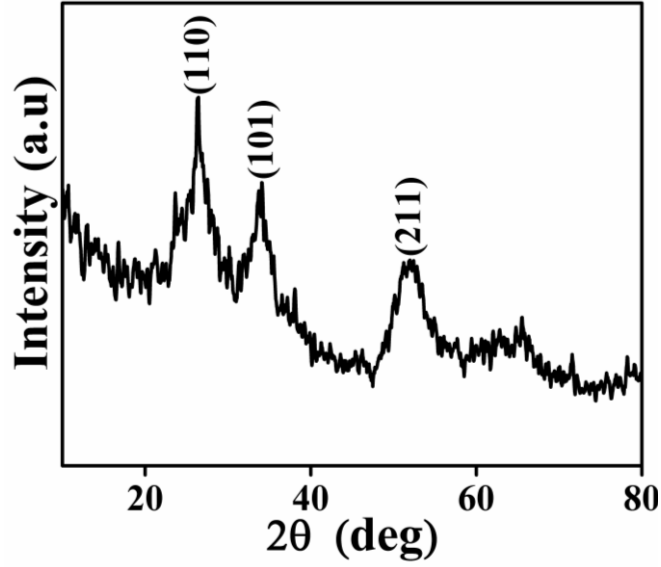
Figure 2: XRD spectrum of SnO$_2$ thin film.

The diffraction peaks appeared at (110), (101) and (211) plane indicates the crystalline face of the SnO$_2$ thin film. The most obvious diffraction peak is along (110) plane and it is the signature of the thin film having good orientation in this plane. From the XRD analysis the presence of SnO$_2$ is confirmed.
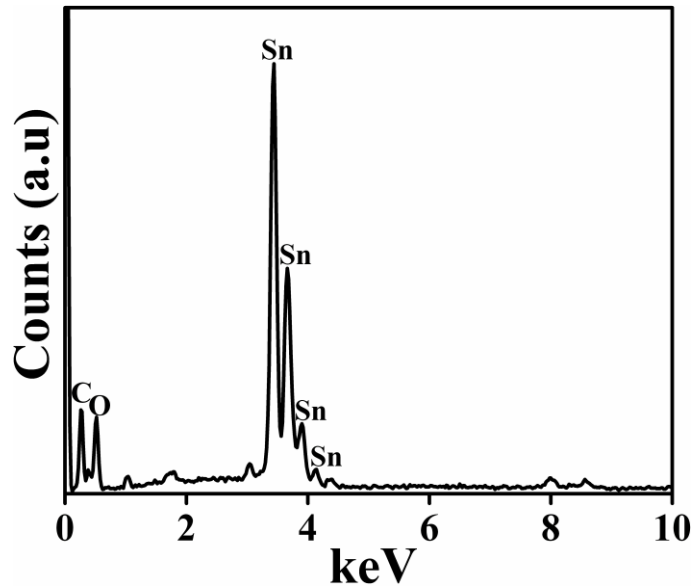
2.3. EDS analysis

Figure 3: ED spectrum of SWCNTs-SnO$_2$ composite.

Figure 3 shows the ED spectrum of SWCNTs-SnO$_2$ composite. The weight percent of the elements present in the SWCNTs-SnO$_2$ composite are 40.37, 36.51 and 23.12 for carbon, oxygen and tin respectively. The presence of carbon in the SWCNTs-SnO$_2$ composite is confirmed by this study.

2.4. CHN-Elemental analysis

It is important to quantify the amount of hydrogen stored in a storage medium. For that, CHN-elemental analysis is carried out using Elementar Vario EL III model analyzer. The hydrogen storage capacities of pure SnO$_2$ and the SWCNTs-SnO$_2$ composite are found to be 0.6 and 2.4 wt.% respectively (with 0.1% error) under the same hydrogenation condition. Hence, one can understand that, three-fourth of hydrogen is stored by SWCNTs in the SWCNTs- SnO$_2$ composite.

2.5. Thermal analysis

To study the desorption behavior, the TG/TDS measurements were carried out using Perkin Elmer-Diamond model unit, over the temperature range 40 - 800°C at a scanning rate of 10°C/min.
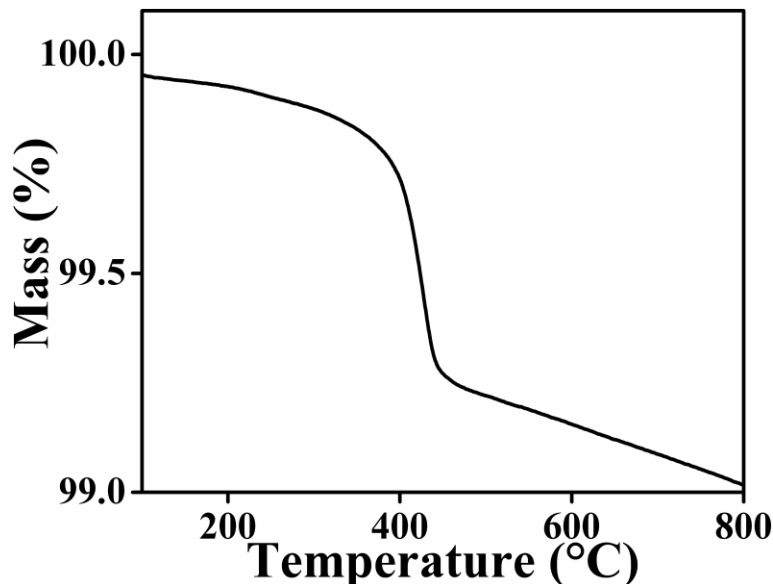

Figure 4: Thermogravimetric spectrum of hydrogenated SnO$_2$ material.

Figure 4 shows the thermo gravimetric spectrum of hydrogenated pure SnO$_2$ sample. It shows the weight loss of about 0.6% over the temperature range 300 - 500°C that corresponds to desorption of stored hydrogen.

Figure 5(a) shows the thermo gravimetric spectrum of hydrogenated SWCNTs-SnO$_2$ composite sample. TG/TDS results reveal a weight loss of about 2.4% in the temperature range 200 - 350°C that corresponds to desorption of stored hydrogen. The presence of SWCNTs in the composite effectively reduces desorption temperature range of hydrogen.
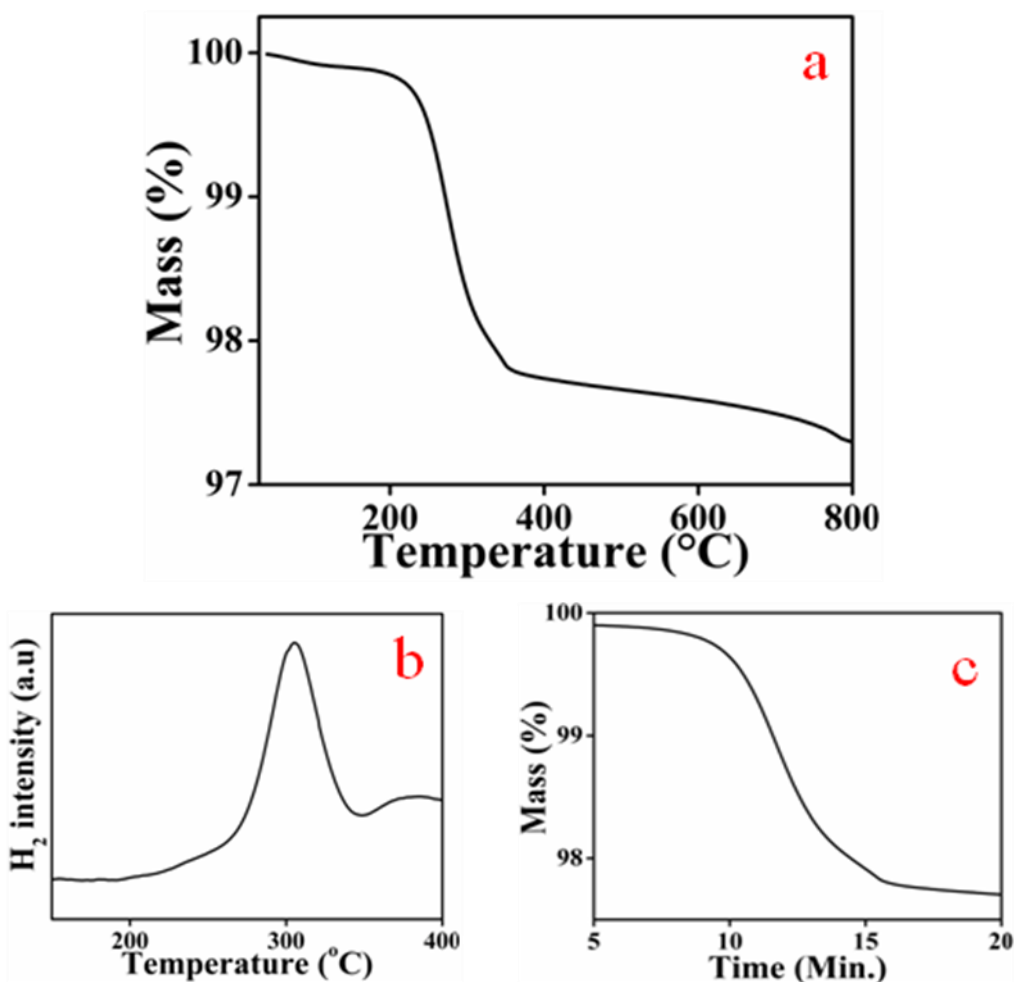
Figure 5: (a) Thermogravimetric spectrum for hydrogenated sample. (b) Hydrogen desorption. (c) Time vs Mass loss spectrum of hydrogenated sample.

Fig. 5(b) shows the behavior of desorption of hydrogen against temperature. It clearly shows that desorption starts above 200°C. Initially, desorption seems to be slow upto the temperature 260°C and after that it changes drastically. A maximum of 1.8 wt.% hydrogen is released at 305°C (desorption peak maximum) and the entire desorption is completed around 350°C. This indicates that more than two-thirds of stored hydrogen is released in the temperature range 200 - 300°C. Fig. 5(c) shows time vs. mass loss spectrum and it indicates that the stored hydrogen is released in approximately 10 min.

From the TG/TDS results, one can infer that the amount of hydrogen desorbed is equal to the amount of hydrogen adsorbed (2.4 wt.%). Thus, our system exhibits 100% desorption in the temperature range, 200 - 350°C in the duration of approximately 10 min. One can control the desorption rate (time) by controlling the scanning rate of desorption temperature.

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The activation energy of desorption, E_d can be calculated from the desorption peak maximum using the following equation [2]

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E_d}{RT_m}$$

where, T_m is the temperature at peak maximum (305°C), β is the heating rate (10°C/min) and R is the universal gas constant. The binding energy of hydrogen is calculated using van't Hoff equation [3] for the desorption temperatures 200, 305 and 350°C and the values are 0.36, 0.45 and 0.49 eV. The corresponding desorption activation energies are 26, 34 and 37 kJ/mol. The recommended binding energy of hydrogen for an ideal hydrogen storage medium lies in the range of 0.2 - 0.4 eV [4]. This range lies between physisorption and chemisorptions limits. The binding energy of hydrogen released in the present work falls in the range of 0.36 - 0.49 eV. Thus, the absorbed hydrogen has both the nature of physical and weak chemical attachment on SWCNTs-SnO$_2$ composite thin film network and importantly the system maintains its stability at room temperature. This indicates the existence of hydrogen binding with different bond strengths due to the different diameters of SWCNTs [5]. The obtained range of the binding energy of hydrogen is far from the pure chemisorption limit. One of the possible reason for the discrepancy in binding energy value is that, during the process of incorporation, initially (in the beginning) the H atoms have lower coverage on the substrate (along with the composite), further as the time of evaporation increases, the coverage of H atoms also increases (that is the available H atoms start to incorporated on the neighboring sites and is go on up to high coverage). This might lead to the formation of H$_2$ molecule upon high coverage. During the course of desorption it desorb as H$_2$ molecules.

3. Conclusion

SWCNTs were successfully deposited with SnO$_2$ material at room temperature in hydrogen atmosphere by electron beam evaporation technique. To the best of our knowledge, this is the first report of hydrogen storage in SWCNTs-SnO$_2$ composite during the preparation of hydrogen medium itself using this technique. The amount of hydrogen incorporated in the composite is found to be 2.4 wt.%. SWCNTs are the responsible for the three-fourth of hydrogen stored in the SWCNTs-SnO$_2$ composite. The thermo gravimetric results reveal that, the entire (100%) stored hydrogen is released in the temperature range 200 - 350°C. The stored hydrogen has both the nature of physical and weak chemical binding on SWCNTs-SnO$_2$ composite thin film network and the system maintains its stability at room temperature.

II. Hydrogenation in Single walled carbon nanotubes-WO₃ Composite

Abstract

The results of hydrogenation of single walled carbon nanotubes (SWCNTs)-WO$_3$ composite thin film is reported here. SWCNTs mixed with WO$_3$ by weight are made into pellet without any binder. Then, the pellet is evaporated by electron beam on glass substrates at room temperature in hydrogen atmosphere. The amount of hydrogen incorporated in the SWCNTs-WO$_3$ composite is found to be 2.7 wt.%. The dehydrogenation behavior is also studied. The experimental evidences are provided by TEM, AFM, SEM, XRD, EDS, CHN and TG/TDS analyses.

1. Experimental

1.1. Composite preparation

SWCNTs are purchased from Sigma Aldrich with the purity of >98%. WO$_3$ material with the minimum assay of 99% is purchased from Merck. The SWCNTs are mixed with WO$_3$ in the ratio of 1:2 by weight. This mixture is grounded well for 15 min. using agate mortar, and is placed in a cylinder-shaped steel mould. Uni-axial pressure of 5 MPa is applied to make them into pellet. Pellet with a diameter of 15 mm and a height of about 5 mm is obtained.

1.2. Film deposition

Glass substrates of dimension 25mm × 75mm × 1.35mm are cleaned with chromic acid, acetone and distilled water by means of sonication for 30 min. The pellet is placed in water cooled graphite crucible and then evaporated in hydrogen atmosphere by electron beam (Hind Hivac Model – 12A4D) on glass substrates at room temperature. The distance between the electron beam source and the substrate is 20 cm. The chamber base pressure is 5×10^{-6} mbar before deposition. The vacuum chamber is flushed with hydrogen gas for 3 min. before evaporation. A beam voltage of 6 kV with the beam current of 15 mA is applied. The hydrogen gas is allowed at a flow rate of 0.5 lit/min. up to the vacuum level 5×10^{-5} mbar during evaporation and the evaporation duration is 15 min.

1.3. Beam production and Hydrogenation

The hydrogen gas is allowed through a regulated valve and gets atomized by thermal cracking produced by tungsten filament. The atomized and excited molecules of hydrogen gas emerge from the valve and impinge on the substrate along with the evaporant and thereby ensure the complete hydrogenation

process. Two set of thin films of pure WO_3 material without hydrogen atmosphere and $SWCNTs-WO_3$ composite in hydrogen atmosphere are prepared under same experimental conditions.

1.4. Characterization

The morphology of SWCNTs is studied by transmission electron microscopy (TEM). The morphology of pure WO_3 and $SWCNTs-WO_3$ composite thin film is studied by atomic force microscopy (AFM). The morphology of pure WO_3 thin film is studied by scanning electron microscopy (SEM). The phases of the WO_3 thin film is studied by X-ray diffraction (XRD) technique. Energy dispersive spectroscopy (EDS) is used to validate the presence of all elements in the $SWCNTs-WO_3$ composite. CHN-elemental analysis is carried out to know the amount of hydrogen incorporated in $SWCNTs-WO_3$ composite thin film. The hydrogen desorption behavior is studied by thermo gravimetric/thermal desorption spectroscopy (TG/TDS) studies.

2. Results and Discussion

2.1. Morphology analysis

The morphology of SWCNTs is imaged by TEM analysis and is shown in Fig. 1(a). The image exhibits the high quality of SWCNTs with the average diameter of around 2 nm. Fig. 1(b) shows AFM image of pure WO_3 thin film. The surface morphology of pure WO_3 thin film is shown in the different magnification of SEM image 1(c) and 1(d). It shows the good distribution of grains with the size in the range of 100 nm. The surface morphology of SWCNTs dispersed in WO_3 thin film shown in the AFM image Fig. 2(a). The AFM image reveals the inclusion of SWCNTs in WO_3 thin film which results in the formation of circular cone protrusions on the smooth WO_3 background. The three dimensional 3D AFM image of $SWCNTs-WO_3$ composite thin film is shown in Fig. 2(b). It shows the formation of the circular cone protrusion with the average height of around 100 nm. The width of the protrusion seems to be around 100 nm.
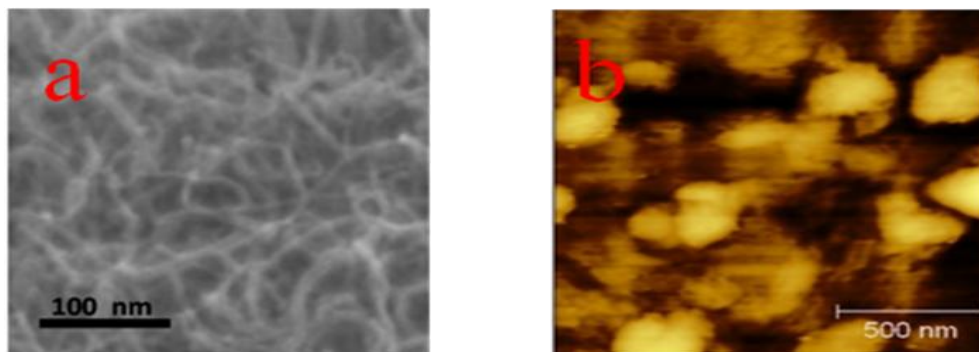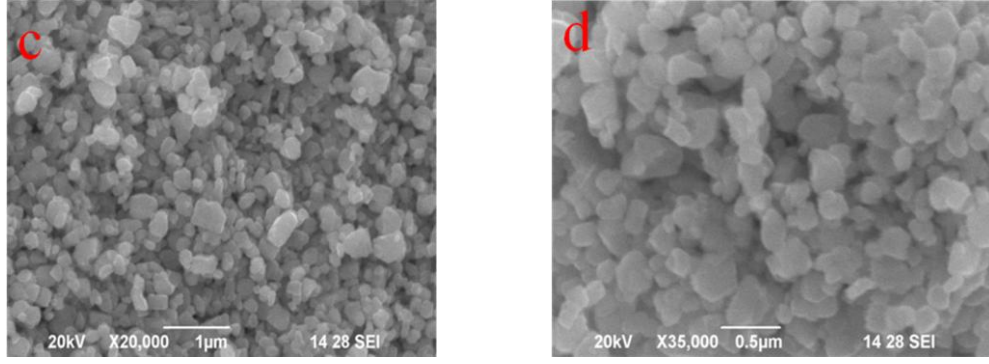
Figure 5: (a) TEM image of SWCNTs. (b) AFM image of WO₃. (c) and (d) show SEM image of WO₃ at different magnifications.
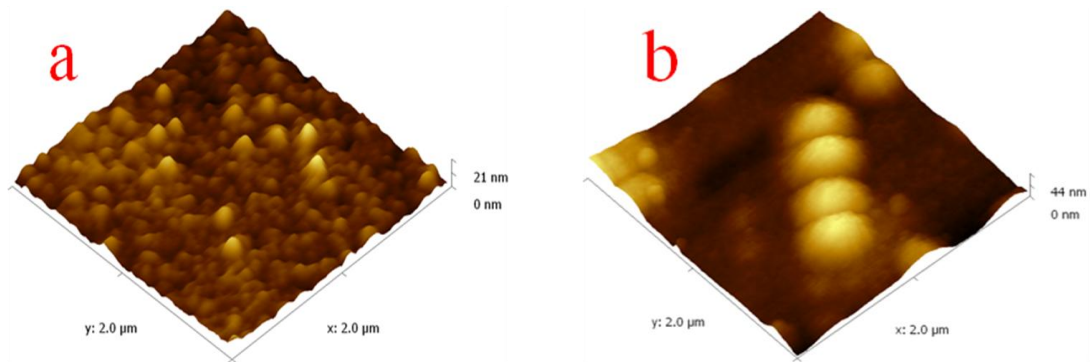

Figure 2: (a) 3D AFM image of SWCNT- WO₃ composite. (b) 3D AFM image focusing circular cone protrusion of SWCNTs formed on the WO₃ background.

The SWCNTs in the composite may be aggregated due to the van der Waals forces to form the circular cone protrusion with the diameter in the obtained range. It is noted that from the AFM images, the CNTs are arranged perpendicularly to the plane of substrate rather the random arrangement on the WO_3 thin film surface. The similar kind of occurrence of circular cone protrusion of MWCNTs on WO_3 thin film background is obtained by Wisitsoraat *et al.* [1]. They pointed out that, the possible reason for this effect is that the CNTs self-organized themselves while they are moving toward substrates in line with the material evaporation trajectory, which is almost perpendicular to the substrate. Thus, the results expose that the deposition of SWCNTs with WO_3 material is possible without any significant decomposition of SWCNTs. Further, the SWCNTs have systematic arrangements on WO_3 thin film with the specific configuration, the circular cone protrusion.

2.2. XRD analysis

X-ray diffraction (XRD) analysis was performed on XPERT-PRO diffractometer operating at 40 kV and 30 mA, using Cu Kα radiation in the scanning range 2θ: 10°−80°. The diffraction pattern of pure WO_3 thin film is shown in Fig. 3.
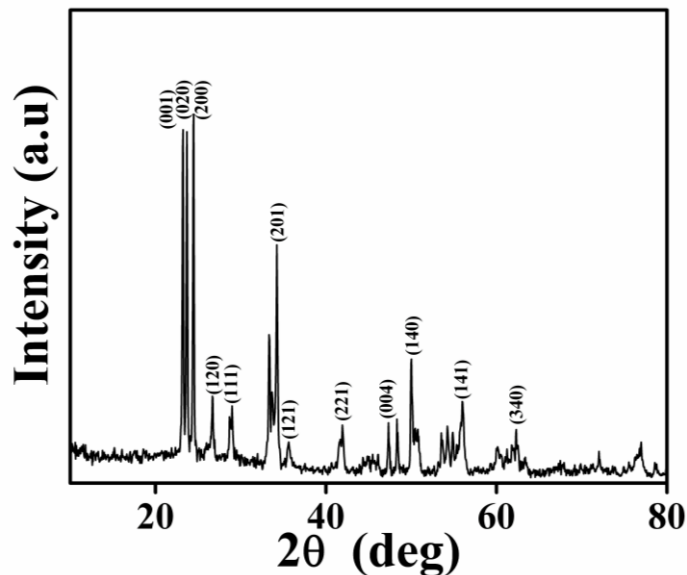

Figure 3: XRD spectrum of WO_3 thin film.

All the diffraction peaks can be well indexed to orthorhombic WO_3. No peaks for other impurities can be detected, indicating the formation of pure WO_3. The sharp peaks suggest that the crystal of WO_3 is perfect. From the XRD analysis the presence of WO_3 is confirmed.
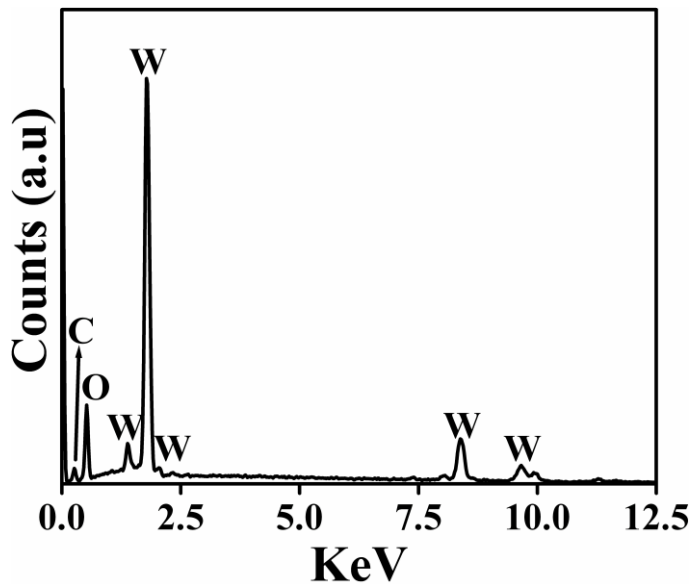
2.3. EDS analysis

Figure 4: ED spectrum of SWCNTs-WO_3 composite.

Figure 4 shows the ED spectrum of SWCNTs-WO$_3$ composite. The weight percent of the elements present in the SWCNTs-WO$_3$ composite are 40.37, 40.51 and 19.12 for carbon, tungsten and oxygen respectively. The presence of carbon in the SWCNTs-WO$_3$composite is confirmed by this study.

2.4. CHN-Elemental analysis

It is important to quantify the amount of hydrogen stored in a storage medium. For that, CHN-elemental analysis is carried out using Elementar Vario EL III model analyzer. The hydrogen storage capacity of SWCNTs-WO$_3$ composite is found to be 2.7 wt.% respectively (with 0.1% error). Hence, the hydrogenation of SWCNTs-WO$_3$ composite is confirmed in this study.

2.5. Thermal analysis

To study the desorption behavior, the TG/TDS measurements were carried out using Perkin Elmer-Diamond model unit, over the temperature range 40 - 800°C at a scanning rate of 10°C/min. Figure 5(a) shows the thermo gravimetric spectrum of hydrogenated SWCNTs-WO$_3$composite sample. TG/TDS results reveal a weight loss of about 2.7% in the temperature range 175 - 305°C that corresponds to desorption of stored hydrogen.
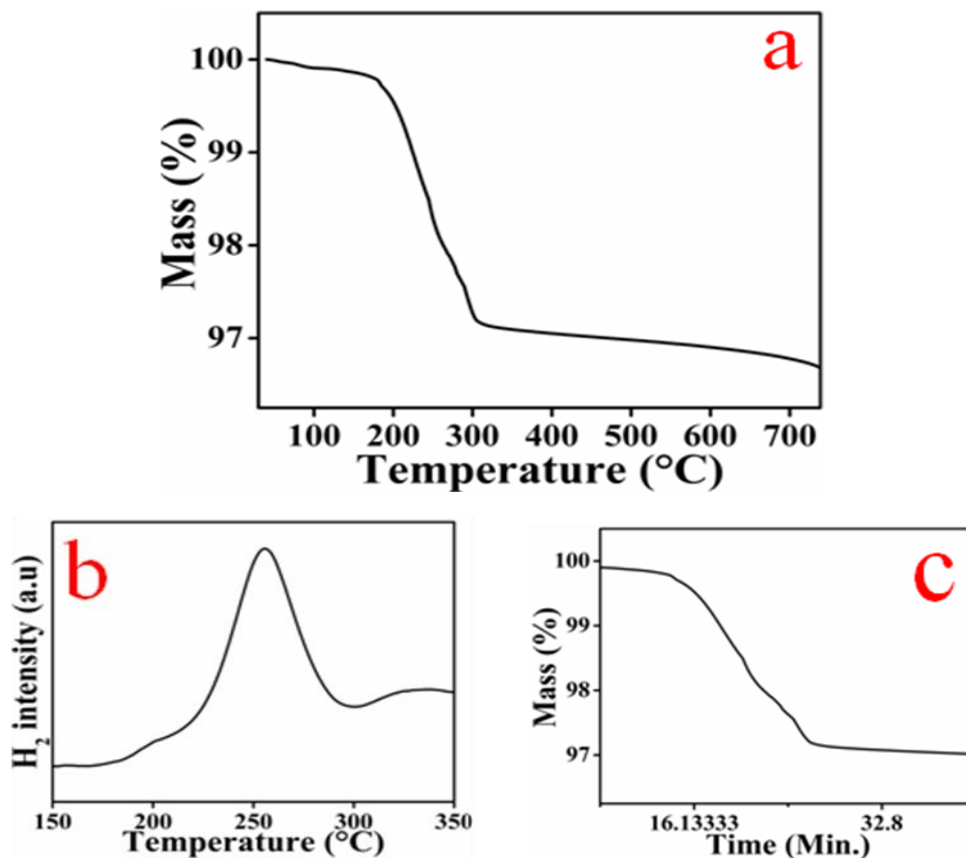

Figure 5: (a) Thermogravimetric spectrum for hydrogenated sample. (b) Hydrogen desorption. (c) Time vs Mass loss spectrum of hydrogenated sample.

Figure 5(b) clearly shows that desorption starts around 175°C. Initially, desorption seems to be slow up to the temperature 220°C and it goes vigorously. A maximum of 2.1 wt.% hydrogen is released at 255°C (desorption peak maximum) and is completed around 305°C. This indicates that more than two - thirds of stored hydrogen is released in the temperature around 250°C. Fig. 5(c) shows time vs. mass loss spectrum and it indicates that the stored hydrogen is released in approximately 10 min.

From the TG/TDS results, one can infer that the amount of hydrogen desorbed is equal to the amount of hydrogen adsorbed (2.7 wt.%). Thus, our system exhibits 100% desorption in the temperature range, 175 - 305°C in the duration of approximately 10 min. One can control the desorption rate (time) by controlling the scanning rate of desorption temperature.

The binding energy of hydrogen is calculated using van't Hoff equation [3] for the desorption temperatures 175, 255 and 305°C and the values are 0.35, 0.41 and 0.45 eV. The corresponding desorption activation energies are 25, 30 and 34 kJ/mol. The recommended binding energy of hydrogen for an ideal hydrogen storage medium lies in the range of 0.2 - 0.4 eV [6]. This range lies between the physisorption and chemisorptions limits. The binding energy of hydrogen released in the present work fall in the range of 0.35 - 0.45 eV. Thus, the absorbed hydrogen has both the nature of physical and weak chemical attachment on SWCNTs-SnO$_2$ composite thin film network and importantly the system maintains its stability at room temperature. This indicates the existence of hydrogen binding with different bond strengths due to the different diameters of SWCNTs [5]. The obtained range of the binding energy of hydrogen is far from the pure chemisorption limit. One of the possible reason for the discrepancy in binding energy value is that, during the process of incorporation, initially (in the beginning) the H atoms have lower coverage on the substrate (along with the composite), further as the time of evaporation increases, the coverage of H atoms also increases (that is the available H atoms start to incorporated on the neighboring sites and is go on up to high coverage). This might lead to the formation of H$_2$ molecule upon high coverage. During the course of desorption it desorb as H$_2$ molecules.

3. Conclusion

SWCNTs were successfully deposited with WO$_3$ material at room temperature in hydrogen atmosphere by electron beam evaporation technique. To the best of our knowledge, this is the first report of hydrogen storage in SWCNTs-WO$_3$ composite during the preparation of hydrogen medium itself using this technique. The amount of hydrogen incorporated in the composite is found to be 2.7 wt.%. The thermo gravimetric results reveal that, the entire (100%) stored hydrogen is released in the temperature range 175 - 305°C. The stored hydrogen has both the nature of physical and weak chemical binding on SWCNTs-WO$_3$ composite thin film network and the system maintains its stability at room temperature.

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III. Hydrogenation in Single walled carbon nanotubes-TiO$_2$ composite

Abstract

The results of hydrogenation of single walled carbon nanotubes (SWCNTs)-TiO$_2$ composite thin film is reported here. SWCNTs mixed with TiO$_2$ by weight are made into pellet without any binder. Then, the pellet is evaporated by electron beam on glass substrates at room temperature in hydrogen atmosphere. The amount of hydrogen incorporated in the SWCNTs-TiO$_2$ composite is found to be 3.2 wt.%. The dehydrogenation behavior is also studied. The experimental evidences are provided by TEM, AFM, XRD, EDS, CHN and TG/TDS analyses.

1. Experimental

1.1. Composite preparation

SWCNTs are purchased from Sigma Aldrich with the purity of >98%. TiO$_2$ material with the minimum assay of 99% is purchased from Merck. The SWCNTs are mixed with TiO$_2$ in the ratio of 1:2 by weight. This mixture is grounded well for 15 min. using agate mortar, and is placed in a cylinder-shaped steel mould. Uni-axial pressure of 5 MPa is applied to make them into pellet. Pellet with a diameter of 15 mm and a height of about 5 mm is obtained.

1.2. Film deposition

Glass substrates of dimension 25mm $\times$ 75mm $\times$ 1.35mm are cleaned with chromic acid, acetone and distilled water by means of sonication for 30 min. The pellet is placed in water cooled graphite crucible and then evaporated in hydrogen atmosphere by electron beam (Hind Hivac Model – 12A4D) on glass substrates at room temperature. The distance between the electron beam source and the substrate is 20 cm. The chamber base pressure is 5x10^{-6} mbar before deposition. The vacuum chamber is flushed with hydrogen gas for 3 min. before evaporation. A beam voltage of 6 kV with the beam current of 30 mA is applied. The hydrogen gas is allowed at a flow rate of 0.5 lit/min. up to the vacuum level 5x10^{-5} mbar during evaporation and the evaporation duration is 15 min.

1.3. Beam production and Hydrogenation

The hydrogen gas is allowed through a regulated valve and gets atomized by thermal cracking produced by tungsten filament. The atomized and excited molecules of hydrogen gas emerge from the valve and impinge on the substrate along with the evaporant and thereby ensure the complete hydrogenation

process. Two set of thin films of pure TiO_2 material without hydrogen atmosphere and SWCNTs-TiO_2 composite in hydrogen atmosphere are prepared under same experimental conditions.

1.4. Characterization

The morphology of SWCNTs is studied by transmission electron microscopy (TEM). The morphology of pure TiO_2 and SWCNTs-TiO_2 composite thin film is studied by atomic force microscopy (AFM). The morphology of pure TiO_2 thin film is studied by scanning electron microscopy (SEM). The phases of the TiO_2 thin film is studied by X-ray diffraction (XRD) technique. Energy dispersive spectroscopy (EDS) is used to validate the presence of all elements in the SWCNTs-TiO_2 composite. CHN-elemental analysis is carried out to know the amount of hydrogen incorporated in SWCNTs-TiO_2 composite thin film. The hydrogen desorption behavior is studied by thermo gravimetric/thermal desorption spectroscopy (TG/TDS) studies.

2. Results and Discussion

2.1. Morphology analysis

The morphology of SWCNTs is imaged by TEM analysis and is shown in Fig. 1(a). The image exhibits the high quality of SWCNTs with the average diameter of around 2 nm. Fig. 1(b) shows AFM image of pure TiO_2 thin film. It shows the good distribution of grains with the average size in the range of 50 nm. The three dimensional 3D AFM image of SWCNTs-TiO_2 composite thin film is shown in Fig. 1(c). The AFM image reveals the inclusion of SWCNTs in TiO_2 thin film which results in the formation of circular cone protrusions on the smooth TiO_2 background. It shows the formation of the circular cone protrusion with the average height of around 100 nm. The width of the protrusion seems to be around 100 nm. The surface morphology of SWCNTs dispersed in TiO_2 thin film at various points shown in the SEM image Fig. 2(a) and 2(b). It shows the cluster formation of TiO_2 grains.
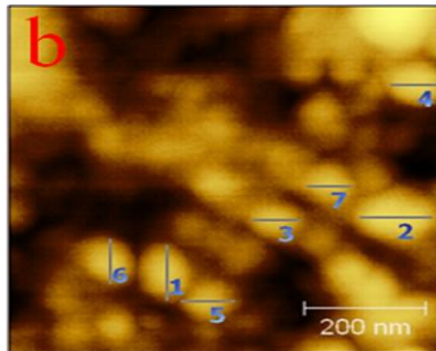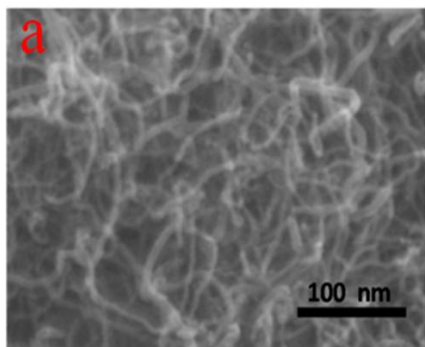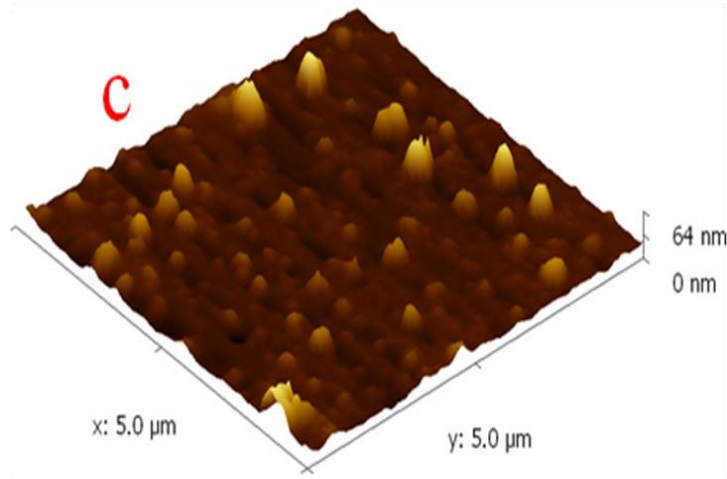
Figure 6: (a) TEM image of SWCNTs. (b) AFM image of TiO$_2$. (c) 3D AFM image of SWCNTs-TiO$_2$ composite.
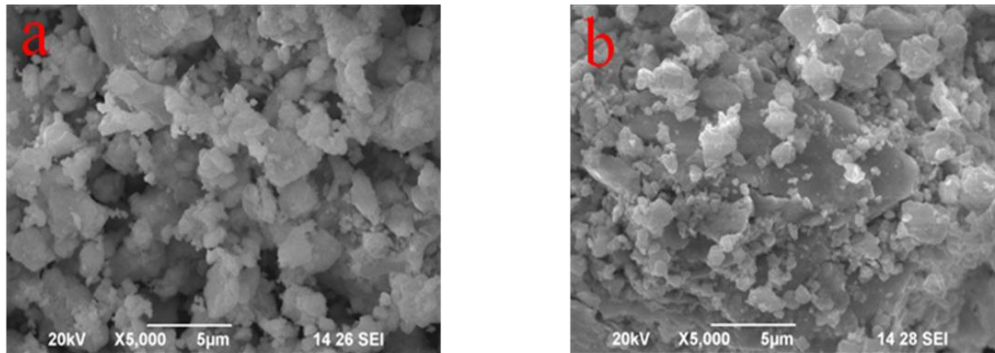

Figure 2: (a) and (b) show SEM images of pure TiO$_2$ clusters at various points.

The SWCNTs in the composite may be aggregated due to the van der Waals forces to form the circular cone protrusion with the diameter in the obtained range. It is noted that from the AFM images, the CNTs are arranged perpendicularly to the plane of substrate rather the random arrangement on the TiO$_2$ thin film surface. The similar kind of occurrence of circular cone protrusion of MWCNTs on TiO$_2$ thin film background is obtained by Wisitsoraat *et al.* [1]. They pointed out that, the possible reason for this effect is that the CNTs self-organized themselves while they are moving toward substrates in line with the material evaporation trajectory, which is almost perpendicular to the substrate. Thus, the results expose that the deposition of SWCNTs with TiO$_2$ material is possible without any significant decomposition of SWCNTs. Further, the SWCNTs have systematic arrangements on TiO$_2$ thin film with the specific configuration, the circular cone protrusion.

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2.2. XRD analysis

X-ray diffraction (XRD) analysis was performed on XPERT-PRO diffractometer operating at 40 kV and 30 mA, using Cu Kα radiation in the scanning range 2θ: 10°−80°. The diffraction pattern of pure TiO_2 thin film is shown in Fig. 3.
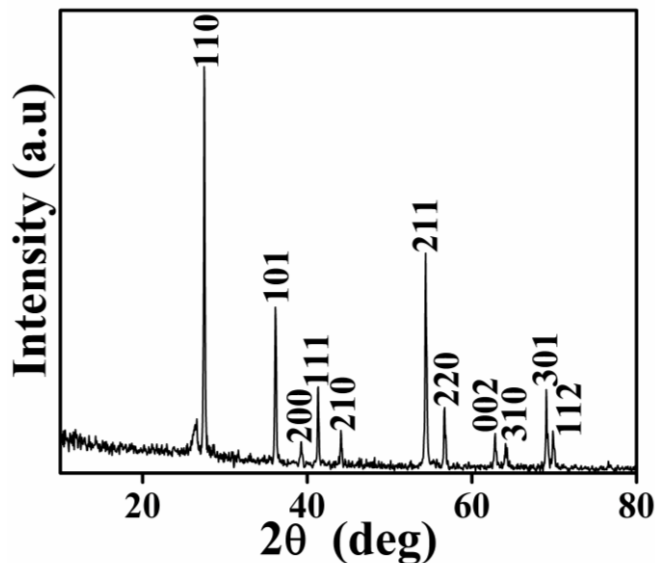

Figure 3: XRD spectrum of TiO₂ thin film.

XRD patterns exhibited strong diffraction peaks at 27°, 36° and 55° indicating TiO_2 in the rutile phase. All the peaks are in good agreement with the standard spectrum (JCPDS no.: 88-1175 and 84-1286). From the XRD analysis the presence of TiO_2 is confirmed.
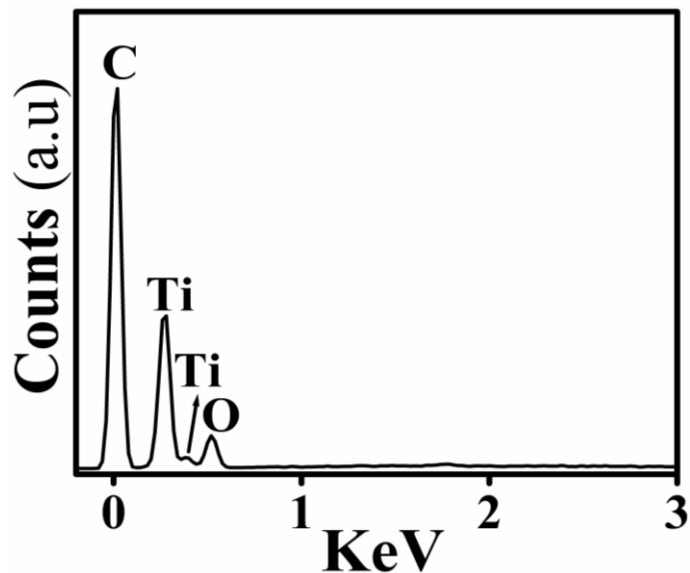
2.3. EDS analysis

Figure 4: ED spectrum of SWCNTs- WO₃ composite.

Figure 4 shows the ED spectrum of SWCNTs-TiO$_2$composite. The weight percent of the elements present in the SWCNTs-TiO$_2$ composite are 63.18, 36.71 and 0.10 for carbon, oxygen and titanium respectively. The presence of carbon in the SWCNTs-TiO$_2$composite is confirmed by this study.

2.4. CHN-Elemental analysis

It is important to quantify the amount of hydrogen stored in a storage medium. For that, CHN-elemental analysis is carried out using Elementar Vario EL III model analyzer. The hydrogen storage capacity of SWCNTs-TiO$_2$ composite is found to be 3.2 wt.% respectively (with 0.1% error). Hence, the hydrogenation of SWCNTs-TiO$_2$ composite is confirmed in this study.

2.5. Thermal analysis

To study the desorption behavior, the TG/TDS measurements were carried out using Perkin Elmer-Diamond model unit, over the temperature range 40 - 800°C at a scanning rate of 10°C/min. Figure 5(a) shows the thermo gravimetric spectrum of hydrogenated SWCNTs-TiO$_2$composite sample. TG/TDS results reveal a weight loss of about 3.2% in the temperature range 150 - 350°C that corresponds to desorption of stored hydrogen.
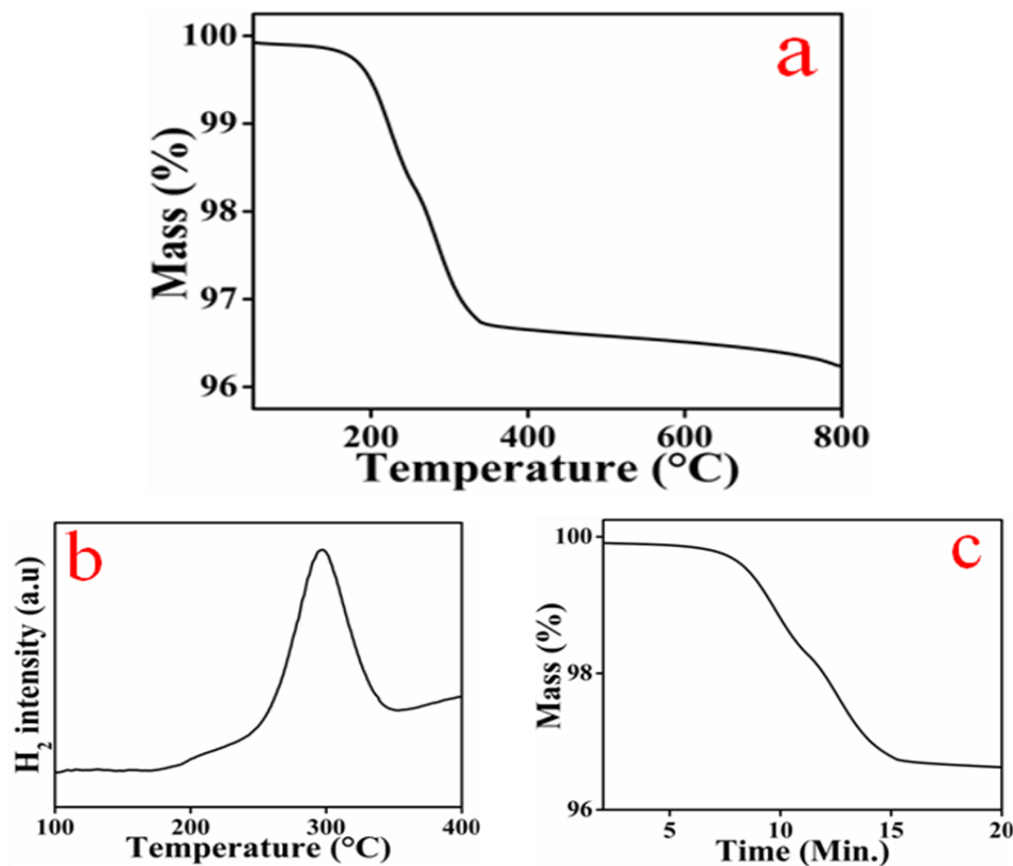

Figure 5: (a) Thermogravimetric spectrum for hydrogenated sample. (b) Hydrogen desorption. (c) Time vs Mass loss spectrum of hydrogenated sample.

Figure 5(b) clearly shows that desorption starts around 150°C. Initially, desorption seems to be slow up to the temperature 180°C and it goes vigorously. A maximum of 2.5 wt.% hydrogen is released at 295°C (desorption peak maximum) and is completed around 350°C. This indicates that more than two - thirds of stored hydrogen is released in the temperature around 300°C. Fig. 5(c) shows time vs. mass loss spectrum and it indicates that the stored hydrogen is released in approximately 10 min.

From the TG/TDS results, one can infer that the amount of hydrogen desorbed is equal to the amount of hydrogen adsorbed (3.2 wt.%). Thus, our system exhibits 100% desorption in the temperature range, 150 - 350°C in the duration of approximately 10 min. One can control the desorption rate (time) by controlling the scanning rate of desorption temperature.

The binding energy of hydrogen is calculated using van't Hoff equation [3] for the desorption temperatures 150, 295 and 350°C and the values are 0.33, 0.44 and 0.49 eV. The corresponding desorption activation energies are 22.7, 33.2 and 37.4 kJ/mol. The recommended binding energy of hydrogen for an ideal hydrogen storage medium lies in the range of 0.2 - 0.4 eV [6]. This range lies between the physisorption and chemisorptions limits. The binding energy of hydrogen released in the present work fall in the range of 0.33 - 0.49 eV. Thus, the absorbed hydrogen has both the nature of physical and weak chemical attachment on SWCNTs-TiO$_2$ composite thin film network and importantly the system maintains its stability at room temperature. This indicates the existence of hydrogen binding with different bond strengths due to the different diameters of SWCNTs [5]. The obtained range of the binding energy of hydrogen is far from the pure chemisorption limit. One of the possible reason for the discrepancy in binding energy value is that, during the process of incorporation, initially (in the beginning) the H atoms have lower coverage on the substrate (along with the composite), further as the time of evaporation increases, the coverage of H atoms also increases (that is the available H atoms start to incorporated on the neighboring sites and is go on up to high coverage). This might lead to the formation of H$_2$ molecule upon high coverage. During the course of desorption it desorb as H$_2$ molecules.

This value is much higher than the storage capacity (0.4 wt.%) reported in ref. 31 for the same composite material prepared by the method of ultrasonication. Hence, the SWCNTs-TiO$_2$ composite prepared by the present method has relatively increased its storage capacity. When compared to the work [7], it is found that the contribution of SWCNTs (from EDS the presence of SWCNTs is 63.18 wt.% in the SWCNTs-TiO$_2$ composite) to the storage capacity is more than TiO$_2$.

The US Department of energy (DOE) have set a target of 5.5 wt.% by 2015 for a storage medium to be used for on-board applications. Though, the maximum storage capacity of our designed storage medium SWCNTs-TiO$_2$ composite thin film is only 3.2 wt.%, one can fine tune the experimental conditions such

as dosage of hydrogen, duration of deposition, concentration of separate components in the composite and different metal oxides to get a higher storage capacity.

3. Conclusion

SWCNTs were successfully deposited with TiO_2 material at room temperature in hydrogen atmosphere by electron beam evaporation technique. To the best of our knowledge, this is the first report of hydrogen storage in SWCNTs-TiO_2 composite during the preparation of hydrogen medium itself using this technique. The amount of hydrogen incorporated in the composite is found to be 3.2 wt.%. The thermo gravimetric results reveal that, the entire (100%) stored hydrogen is released in the temperature range 150 - 350°C. The stored hydrogen has both the nature of physical and weak chemical binding on SWCNTs-TiO_2 composite thin film network and the system maintains its stability at room temperature.

References

[1] Wisitsoraat A, Tuantranont A, Thanachayanont C, Patthanasettakul V and Singjai P. Electron beam evaporated carbon nanotubes dispersed SnO_2 thin film gas sensor. J Electroceram 2006;17:45-9.

[2] Ioannatos GE and Verykios XE. H_2 storage on single- and multi-walled carbon nanotubes. Int J Hydrogen Energy 2010;35:622-8.

[3] Durgun E, Ciraci S and Yildirim T. Functionalization of carbon-based nanostructures with light transition–metal atoms for hydrogen storage. Phys Rev B 2008;77:085405 (9 pp).

[4] Lochan RC and Head-Gordon M. Computational studies of molecular hydrogen binding affinities: The role of dispersion forces, electrostatics, and orbital interactions. Phys Chem Chem Phys 2006;8:1357-70.

[5] Park S, Srivastava D and Cho K. Generalized Chemical Reactivity of Curved Surfaces: Carbon Nanotubes. Nano lett 2003;3:1273-7.

[6] Nikitin A, Li X, Zhang Z, Ogasawara H, Dai H and Nilsson A. Hydrogen storage in carbon nanotubes through the formation of stable C-H bonds. Nano lett 2008;8:162-7.

[7] Rather S, Mehraj-ud-din N, Zacharia R, Hwang SW, Kim AR and Nahm KS. Hydrogen storage of nanostructured TiO_2-impregnated carbon nanotubes. Int. J. Hydrogen Energy 2009;34:961-6.

[8] Silambarasan D, Surya VJ, Vasu V and Iyakutti K. Experimental investigation of hydrogen storage in single walled carbon nanotubes functionalized with borane. Int J Hydrogen Energy 2011;36:3574-9.

[9] Hydrogen adsorption/desorption in functionalized single-walled carbon nanotubes

D. Silambarasan, V. Vasu, V. J. Surya, and **K. Iyakutti, AIP Conf. Proc. 1447, 253-254 (2012).**

[10] Investigation of hydrogen desorption from hydrogenated single-walled carbon nanotubes
functionalized with borane
D. Silambarasan, V. Vasu, V. J. Surya and **K. Iyakutti**
IEEE- Transactions on Nanotechnology(2012)DOI 10.1109/TNANO.2012.2211383(in press)

Appendix

A. Personal Supported: i) D. Silambarasan
ii) Dr. V. Vasu
ii) V.J. Surya

B. Papers published in international journal:

1. D. Silambarasan, V. Vasu, V. J. Surya and K. Iyakutti, Investigation of Hydrogen
   Desorption From Hydrogenated Single-Walled Carbon Nanotubes Functionalized With
   Borane, *IEEE TRANSACTIONS ON NANOTECHNOLOGY,*
   DOI: 10.1109/TNANO.2012.2211383 (in Press)

Papers to be submitted to international journal:

1. D. Silambarasan, V. Vasu, K. Iyakutti and V. J. Surya, Hydrogenation in Single walled
   carbon nanotubes-SnO_2 composite.
2. D. Silambarasan, V. Vasu, K. Iyakutti and V. J. Surya, Investigation of Single walled
   carbon nanotubes-WO_3 composite as a hydrogen storage medium.
3. D. Silambarasan, V. Vasu, K. Iyakutti and V. J. Surya, Hydrogen adsorption and desorption
   in Single walled carbon nanotubes-TiO_2 composite.

Papers Presented in Conferences:

1. D. Silambarasan, V. J. Surya, V. Vasu, and K. Iyakutti, Desorption studies on hydrogenated
   single walled carbon nanotubes functionalized with borane (BH_3), International Conference
   on Nanoscience and Nanotechnology, Coimbatore Insititute of technology, Coimbatore,
   July 6-8, 2011.

2. D. Silambarasan, V. Vasu, V. J. Surya and K. Iyakutti, Hydrogen Adsorption/Desorption in
   Functionalized Single-Walled Carbon Nanotubes, 56th DAE Solid State Symposium, SRM
   University, Chennai, Dec. 19-23, 2011.

3. D. Silambarasan, V. Vasu, V. J. Surya and K. Iyakutti, Hydrogen storage in single walled
   carbon nanotubes-metal oxide composites, National Conference on Physics of New
   Materials, Noorul Islam University, April 20-21, 2012.

Conferences proceedings published in net:

1. D. Silambarasan, V. J. Surya, V. Vasu, and K. Iyakutti, Desorption studies on hydrogenated single walled carbon nanotubes functionalized with borane (BH_3), *Journal of Nano Research Special Volume of Dr. Velumani, Article ID: 14.139.186.2-11/07/12,12:38:38 (In Press)* **[Impact Factor = 0.577].**

2. D. Silambarasan, V. Vasu, V. J. Surya and K. Iyakutti, Hydrogen Adsorption/Desorption in Functionalized Single-Walled Carbon Nanotubes, 56th DAE Solid State Symposium, SRM University, Chennai, Dec. 19-23, 2011, *Solid State Physics, AIP Conf. Proc. 1447, 253-254 (2012); doi: 10.1063/1.4709975.*

Papers to be presented in Conference:

1. D. Silambarasan, V. Vasu, K. Iyakutti and V. J. Surya, Hydrogenation and Dehydrogenation in Single-Walled Carbon Nanotubes-TiO_2 composite, *57th DAE Solid State Symposium, IIT Bombay, Bombay, Dec. 3-7, 2012.*

Interactions:

1. Desorption studies on hydrogenated single walled carbon nanotubes functionalized with BH3
   D. Silambarasan, V. J. Surya, V. Vasu, and **K. Iyakutti**
   International Conference on Nanoscience and Nanotechnology, CIT, Coimbatore, July 6-8, 2011.

2. Hydrogen storage in single walled carbon nanotubes functionalized with hydrides
   K. Iyakutti
   International Conference on Advanced Materials (ICAM – 2011),
   PSG College ofTechnology, Coimbatore, India, December 12-16, 2011.

D. Inventions: None

E. Honors/ Awards : D. Silambarasan, V. Vasu, V. J. Surya and K. Iyakutti, Hydrogen Adsorption/Desorption in Functionalized Single-Walled Carbon Nanotubes - Best Poster Award in 56th DAE Solid State Symposium held at SRM University, Chennai, during Dec. 19-23, 2011.

F. Archival Documentation: PDF of the Preprint of the submitted paper is attached to the Report.

90% of the proposed work is completed.